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FLOW INJECTION ANALYSIS CONCEPTS AND MISCONCEPTIONS

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Abstract

Aspects of definitions of analytical chemistry and flow injection analysis are discussed. The driving force in analytical research of cost-effectiveness is identified and the characteristics of flow injection examined. Basic concepts of fluid flow relevant to flow injection are explained and some common misconceptions concerning the magnitude of various phenomena examined. The implications for the design of manifolds for high sensitivity are evaluated and some practical problems addressed. Novel features of FI, which take advantages of the kinetic nature of suitable processes, are identified and illustrated by some of Professor Ishibshi's work.

From a pedagogical viewpoint, it is desirable to be able to classify analytical chemistry techniques and procedures as this provides a sensible way of presenting material to students. It is agreed that the acquisition of knowledge is easier if the material to be learned has a coherent structure and framework. What the well-regarded teachers of analytical chemistry regard as an appropriate framework may be ascertained from a perusal of the contents pages of any modern text book [1,2]. A criticism that maybe levelled at all such texts is that the overall philosophy of analytical chemistry is hardly mentioned at all. This may be because of space constraints and also because there is some debate about what this philosophy is and even about what analytical chemistry is.

A series of articles, being the prize winning entries of a competition held under the direction of Professor Manfred Grasserbauer, have addressed the issue of the definition of analytical chemistry [3,4,5,6] and illustrate that there is still some variation between the thinking of the world's leading exponents of the discipline. A more prosaic definition has been discussed by Tyson [7], namely that analytical chemistry is "what analytical chemists do", a definition which has both its supporters

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1. D. C. Harris, *Quantitative Chemical Analysis*, 2nd. ed., Freeman, New York (1987).
 2. D. A. Skoog, D. M. West and F. J. Holler, *Fundamentals of Analytical Chemistry*, 6th ed., Saunders, Fort Worth, 1992.
 3. K. Camman, *Fresenius' J. Anal. Chem.*, **343**, 812 (1992).
 4. M. Valcarcel, *Fresenius' J. Anal. Chem.*, **343**, 814 (1992).
 5. A. M. Zuckerman, *Fresenius' J. Anal. Chem.*, **343**, 817 (1992).
 6. Zhou Nan, *Fresenius' J. Anal. Chem.*, **343**, 819 (1992).
 7. J. F. Tyson, *Analyst*, **115**, 881 (1992).

[8,9] and its critics [10]. What many of the less pragmatic definitions overlook is that the practice of analytical chemistry involves the provision of chemical information relevant to the problem to be solved. It is the practice of analytical chemistry which to a large extent provides the driving force for research and academic analytical chemists should not lose sight of this.

A major motivating factor for analytical chemistry research and development is the requirement to make analytical methods more cost effective. If the figures quoted by Hertz [11] are at all accurate (of the 250 million chemical measurements made each day in the USA, 1 in 10 have to be repeated because of suspected contamination, interference or poor result), then a disturbing picture of the current state of the practice of analytical chemistry emerges. As the estimated annual cost of these repeat analyses is \$50 billion, it is clear that making analytical measurements more cost-effective is a non-trivial goal.

One deduction from Hertz's figures is that there must be large numbers of chemical measurements made by persons other than analytical chemists, no matter how broad a definition of analytical chemist one chooses. This would certainly add weight to the argument that there is a need for more scientific personnel trained as analytical chemists. However, the figures also mean that there is a clear need for the existing methodology to be more robust, even allowing for the fact that (a) the method being used may be inappropriate and (b) the personnel involved may be unaware of the possible sources of systematic error. In turn these considerations lead to the formulation of some criteria for the evaluation of analytical methodology, namely the degree of robustness and the degree to which the procedure is free from bias.

Improvements in Analytical Method Performance

Thus in addition to the well-known criterion of greater detection power and greater selectivity, several criteria related to cost-effectiveness should be considered when evaluating the results of research designed to improve analytical chemistry methodology. In addition to freedom from contamination and ruggedness, it is clear that speed of analysis is important. Reduction in reagent consumption and in the generation of waste disposal problems are also important.

Flow Injection Procedures

Just as there are problems of providing a definition of analytical chemistry when viewed from an external viewpoint, there are also some difficulties with topics within the subject area. One such topic is "flow injection analysis" for which several of the leading practitioners have attempted to

8. T. Braun, *Anal. Proc.*, **30**, 216 (1993).
9. C. N. Reilley, *Spectroscopy*, **5**, 20 (1990).
10. H. Malissa, *Fresenius' J. Anal. Chem.*, **343**, 814 (1992).
11. H. S. Hertz, *Anal. Chem.*, **60**, 75A (1988).

provide definitions [12,13,14]. As has been pointed out previously [15], it is difficult to formulate a definition of flow injection analysis that does not include the instrumental chromatographies (GLC and HPLC) and that no matter how broad the terms of the definition, it will always be possible to find examples that do not fall within the boundaries so set.

Basic Concepts

The common feature of all flow injection (FI) methods is that the characteristics of fluid flow in closed conduits are exploited for one or more of the following operations on a controlled amount of sample (a) the transport of samples, (b) the chemical pretreatment of samples and (c) the presentation of samples to a chemical instrument. Fluid flow and the associated hydrodynamic processes are inherently reproducible and thus sample manipulations by fluid flow are precise. This is important as FI methods are serial, i.e. samples and standards are handled sequentially. As all samples and standards have identical residence times, the kinetic limitations of conventional analytical methods, in which samples and standards are handled in parallel, do not apply. Thus it is not necessary for any of the chemical or physical processes in the system to be at equilibrium and restrictions on the stability of both the product and the reagents can be relaxed. This aspect of FI will be discussed in more detail later.

Open Tubular Single Line Manifold

Explanations of the basics of FI often start with a description of the single line manifold (SLM) in which a reagent carrier stream continuously flows and into which a discrete volume of sample solution is injected. However, the limitations of static illustrations in text books and manufacturers' literature often perpetrate misconceptions at this early stage. Although it is correctly stated that the resulting shape of the dispersed sample zone is due to the combination of laminar flow (in which a parabolic velocity profile develops between the center stream line and the wall) and diffusion, the magnitude of these processes are often underestimated.

In a laminar flow regime, the center streamline flows at twice the average linear velocity. For a conduit of internal diameter d mm in which fluid flows at Q ml min⁻¹, the center stream line travels at $42.4Q/d^2$ mm s⁻¹. That is for the typical values of $Q = 1$ ml min⁻¹ and $d = 0.5$ mm, the center stream line is moving at 170 mm s⁻¹. This is faster than is expected, as most analytical chemists have only seen fluid flow in closed conduits in autoanalyser systems where the linear velocity is much slower because of the much larger internal diameter of the tubing. Ideas about the shape of the sample zone also seem to be carried over from this methodology, as the dispersing sample zone

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12. J. Ruzicka and E. H. Hansen, *Flow Injection Analysis*, 2nd ed., Wiley, New York, (1988), p. 380.
 13. M. Valcarcel and M. D. Luque de Castro, *Flow Injection Analysis. Principles and Applications*, Ellis Horwood, Chichester (1987), Ch. 2.
 14. Z. Fang, *Micochem. J.*, **45**, 137 (1992).
 15. J. F. Tyson, *Spectrochim. Acta Rev.*, **14**, 169 (1991)

is often drawn as a hollow bullet, whereas in reality it is an elongated hollow needle, as may be readily demonstrated [16,17]. The initial length of the sample zone is also underestimated in many illustrations. For an injection volume V_i μl , the length occupied in a tube of internal diameter d mm is $1.27V_i/d^2$. For $V_i = 100$ μl and $d = 0.5$ mm, the length of tubing occupied by the sample (i.e. the length of the loop of an injection valve) is 509 mm. The difficulties of scale drawing of the cross section of typical flow injection tubing now become apparent. It should be considered that any illustration of the flow injection experiment which attempts to visualize dispersion processes is drawn to at least two different scales on the same diagram.

Dispersion and Mixing

Laminar Flow

It is often stated that in a SLM, dispersion is a consequence of laminar flow and diffusion. The effects of laminar flow are commonly referred to as convection in the flow injection literature, but it should be borne in mind that "convection" is merely a term for the enthalpy flux due to fluid flow [18] and is not reserved for the particular case of the laminar flow of an incompressible fluid in a closed circular pipe. The parabolic velocity gradient which develops as a consequence of laminar flow does not, in itself, result in any mixing. The concentration profile recorded at a downstream non-invasive detector would show a profile rising sharply from zero to a maximum followed by a long trailing edge, because any real detector of this sort integrates the concentration in a defined volume. If it were possible to sense the concentration in any particular stream line, then the profile for laminar flow only would be rectangular.

Such considerations of detector mode have important practical consequences. There is a small but sustained interest in the development of a theory of dispersion and reaction in flow injection. One of the goals of such a theoretical treatment is the derivation of equations which predict the extent of dispersion as a function of relevant experimental parameters. However any approach which treats concentration as a mathematical function only will never be successful as, in the real world, "concentration" at a point or in a plane is meaningless. Concentration only has meaning when the volume considered is large compared with the size of the entities in the fluid, so that the effects of Brownian motion are negligible. And as has just been pointed out, real detectors integrate over a substantial volume (even those based on "surface" electrochemical phenomena).

Although the parabolic velocity gradient is alluded to it is rarely illustrated by an appropriate plot. This is rectified in Fig. 1, which shows the relationship between linear velocity and distance

16. J. F. Tyson, *Fresenius' Z. Anal. Chem.*, **329**, 675 (1987)
17. I. D. McKelvie, T. J. Cardwell and R. W. Cattrall, *J. Chem. Educ.*, **67**, 262 (1990).
18. W. L. McCabe, J. C. Smith and P. Harriott, *Unit Operations of Chemical Engineering*, 4th ed., McGraw-Hill, New York, 1985.

from the tube wall up to the center of the tubing. The significance of this is that it shows the difference in the velocity change due to radial movement for molecules in the center and molecules at the wall. This movement of the molecules is always present in fluids, but it usually ignored because for a homogeneously mixed solution, there are no changes in bulk concentrations as a function of time.

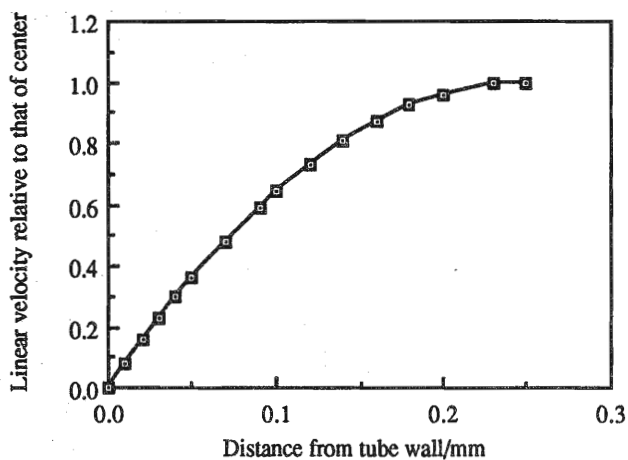


Fig. 1. Relationship between linear velocity and distance from tube wall in a laminar flow regime.

Diffusion

Any given individual molecule is moving in a random fashion mainly due to collisions with solvent molecules, the effects of which are to smooth out any concentration gradients. It is not possible to specify how fast any given molecule will move under this random thermal agitation, it is only possible to describe the bulk effect. The bulk effects of this motion are described by Fick's laws of diffusion, which feature prominently in theories of transport to electrode surfaces and of flow injection dispersion. It would be useful to know how fast a concentration boundary moves under the action of diffusion.

There are various ways in which this can be visualized. A useful model for the process is to consider the one-dimensional movement of species from a region of high concentration to one of low concentration to be the movement of a sharp boundary behind which the concentration is equal to that of the higher value and beyond which the concentration is equal to the lower value. This model requires that there is a sufficiently large reservoir of the more concentrated solution so that during the time of observation, the higher concentration does not change (i.e. the process is referred to as semi-infinite linear diffusion). This is illustrated in Fig. 2.

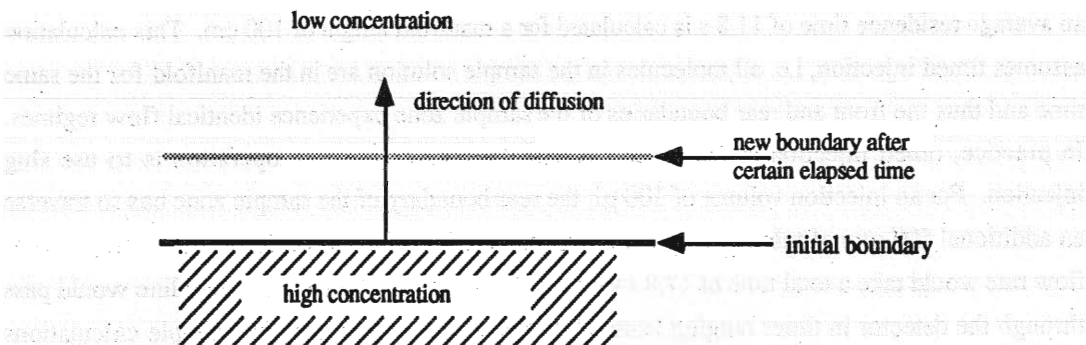


Fig. 2 Movement of concentration boundary under semi-infinite linear diffusion conditions

This boundary moves out into the solution so that the distance moved is given by $2(D_m t / \pi)^{1/2}$ [19]. Where D_m is the molecular diffusion coefficient. This boundary does not move with a uniform velocity but the distance travelled may be readily calculated from the formula and for a typical value of $D_m = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, values are shown in Fig. 3.

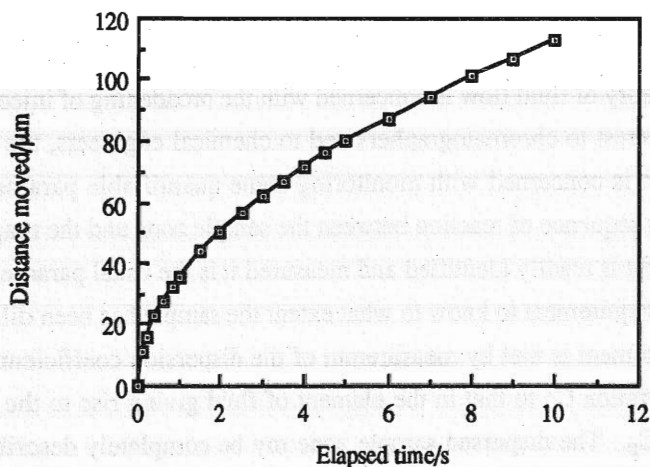


Fig. 3. Distance travelled by diffusion boundary as a function of time for semi-infinite linear diffusion.

Residence Times

To determine the time available for diffusion effects, it is necessary to make some estimates of residence times in a flow injection system. As the average linear velocity is $21.2Q/d^2 \text{ mm s}^{-1}$, the average residence time (in seconds) of a sample molecule for a length of tubing, $L \text{ cm}$, between the injection valve and the detector is given by $0.472d^2L/Q$. For the values of d and Q used previously

19. J. F. Tyson and T. S. West, *Talanta*, 27, 335 (1980).

an average residence time of 11.8 s is calculated for a manifold length of 100 cm. This calculation assumes timed injection, i.e. all molecules in the sample solution are in the manifold for the same time and thus the front and rear boundaries of the sample zone experience identical flow regimes. In practice, timed injection is the exception and the normal mode of operation is to use slug injection. For an injection volume of 100 μl , the rear boundary of the sample zone has to traverse an additional 509 mm of tubing. A molecule on the rear boundary travelling at the average linear flow rate would take a total time of 17.8 s to reach the detector. The center stream line would pass through the detector in times ranging from 5.9 to 8.9 s. It is clear from these simple calculations and from Fig. 3. that during residence in the flow manifold, molecules could diffuse distances of the order of 100 μm . From Fig. 1 it may be seen that a molecule in the center stream line which moved 100 μm towards the wall would suffer a decrease in velocity to 84% of the maximum, whereas a molecule which moved from the wall 100 μm towards the center would increase its velocity from 0 to 64% of the maximum. The effect of diffusion is to slow down the front of the laminar flow profile slightly and speed up the rear of the profile considerably.

Although diffusion in liquids is considered a slow process (which it is compared with diffusion in gases), it is rapid enough so that molecules in a typical flow injection system can diffuse substantial fractions of the tube radius in the residence time in the system.

Dispersion Coefficient

Although much of the theory of fluid flow is concerned with the broadening of injected zones, as this is of considerable interest to chromatographers and to chemical engineers, the analytical application of flow injection is concerned with monitoring some quantifiable parameter of the product peak formed as a consequence of reaction between the sample zone and the reagent in the carrier stream. As peak height is readily identified and measured it is the usual parameter chosen and thus it is a fundamental requirement to know to what extent the sample has been diluted at the peak maximum. This requirement is met by measurement of the dispersion coefficient being the ratio of the injected concentration C_0 to that in the element of fluid giving rise to the analytical readout, C_p . Thus $D = C_0/C_p$. The dispersed sample zone may be completely described by the variation of the "dispersion coefficient" at any point on the concentration gradient, D_g , with time so that $D_g = C_0/C_g$.

Dispersion coefficient is of such fundamental importance that no publication in which a FI system is described should appear in the research literature unless the appropriate values of D are given. Unfortunately, this happens quite often.

The dispersion coefficient is usually considered to be a sample property (and for good reasons to be discussed below) but there is, for the SLM, a simple relationship between the dispersion coefficient of the sample and that of the reagent in the carrier stream, D^r namely that $D^r = D/(D - 1)$ [20]. It is useful to plot D^r as a function of D as an aid in optimizing manifold design. This plot is shown in Fig. 4.

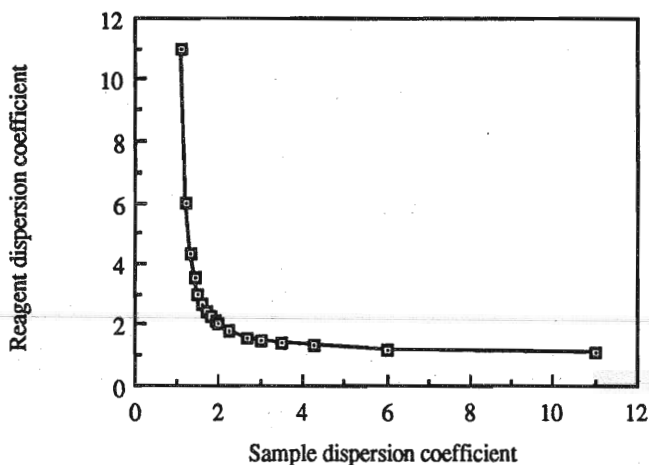


Fig. 4. Relationship between D^r and D

Dispersion Coefficient and Optimization

Often the main requirement of a flow injection system is the maximum sensitivity for a procedure involving on-line reaction. Clearly the sample dispersion coefficient should be minimized, but the consequence of this is that the reagent dispersion coefficient may become very large (see Fig. 4) and there will not be enough reagent to cause the product to be fully formed. If kinetic considerations were not important, it would seem that the optimization strategy should consist of constructing a manifold which produces the desired stoichiometric ratio of reagent to sample at the peak maximum while minimizing sample dispersion. Often it appears that the desired ratio is not known, as many optimization studies include reagent concentration as a parameter to be varied. It should be clear that the initial approach would be to maximize the reagent concentration and then to obtain a dispersion coefficient such that for the most concentrated standard there is equivalence between the sample and reagent at the peak maximum. For a 1:1 stoichiometry, a formation constant (K) of 10^8 is needed to get 99.9% conversion of a 10^{-2} M sample solution. For trace analytical purposes the sample concentration may be considerably lower and thus the value of K needed for 99.9% reaction is diminished accordingly.

20. J. F. Tyson, *Anal. Chim. Acta*, 179, 131 (1986).

If the ratio of sample to reagent concentrations at the peak maximum is to be 1:1, it is possible to calculate what the ratio of the injected concentration to carrier stream concentration should be as a function of D [20]. In general, the relationship is $R_0 = R_p/(D - 1)$. Where R_0 is the concentration ratio of reagent in carrier to injected sample concentration and R_p is the concentration ratio at the peak maximum.

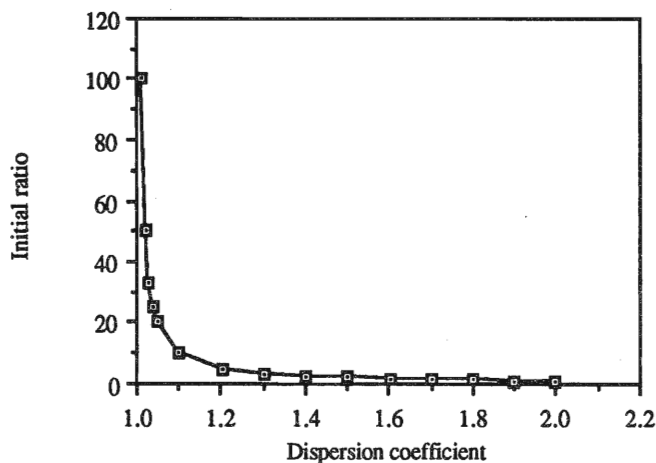


Fig 5. Concentration ratio of reagent to standard to give a peak ratio of 1:1.

It is easily seen from this graph that if high initial concentration ratios of reagent to sample are possible, the manifold should have a dispersion coefficient close to 1. For some reason this design criteria is never adopted and the almost universal practice is to use D values of 2 - 3 or even higher.

Precision of Low Dispersion Coefficient Values

One possible reason for not designing manifolds with such low dispersion coefficient values is that small changes in operating parameters could produce unacceptable variations in peak height precision. It is readily seen that C_p varies approximately linearly with D , so the consideration is whether small changes in an operating parameter (volume injected is the most obvious candidate) could cause unacceptable changes in D . The effect of V_i on D may be conveniently calculated from the single-well stirred tank for dispersion behavior as it is well known that the relationship between D and V_i is exponential [21]. Suppose the dispersion characteristics as far as peak height are concerned can be modelled by plug flow though a mixing chamber of V μ l volume then $D = [1 - \exp(-V_i/V)]^{-1}$ and thus to obtain a D value of 1.005 for a V of 100 μ l, an injection volume of 530

21. J. Ruzicka and E. H. Hansen, *Flow Injection Analysis*, 2nd ed., Wiley, New York (1988), p. 26

μl is needed. If this value changes by $\pm 5 \mu\text{l}$ the dispersion coefficient changes from 1.0048 to 1.0053. These changes are not significant in terms of sample peak height but the reagent to sample ratio changes from 0.96 to 1.06, which is significant in terms of product peak height. Once the ratio has fallen below 1, double peaks will form.

Avoiding Double Peaks

One way to avoid double peak formation is to move away from the conditions required for maximum sensitivity and work with a higher ratio of reagent to sample at the peak maximum. An alternative approach is to use a different design of manifold in which mixing is not by diffusion but by the turbulence produced at and/or downstream of a confluence point. This second type of manifold, the double line manifold, is normally used in the mode in which the sample is injected into an inert carrier stream which then merges with the continuously pumped reagent stream at the confluence point.

The conventional wisdom would appear to be that this design is inherently more sensitive than the single line manifold because no matter how large a volume is injected, double peaks do not form [22]. It is considered that double peak formation limits the sensitivity obtainable with the single line manifold. However, this is not the case. Leaving kinetic limitations aside, when the experimental procedure consists of diluting the sample with the reagent solution, maximum sensitivity will be obtained under one unique set of conditions. For the two manifolds the experimental conditions will be different, notably in terms of the volume injected and for the double line it is clear that the reagent flow will be minimized in relation to the sample flow so as to minimize sample dilution. It is also clear that the reagent concentration should be maximized.

A third manifold configuration, known as "reverse flow injection", has been described as a means of increasing the sensitivity [23] and is also discussed in the text-books as a design of inherently high sensitivity. This is a SLM in which the reagent is injected into the sample which forms the carrier stream. However, the same argument applies to this design as to the other two. If the reagent concentration is maximized then maximum sensitivity will be achieved under a unique set of conditions corresponding to the optimum mutual dilution of sample and reagent. This misconception of the high sensitivity design has been pointed out on previous occasions [24,25] and has recently been proved experimentally [26].

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22. M. Valcarcel and M. D. Luque de Castro, "Flow Injection Analysis. Principles and Applications", Ellis Horwood, Chichester (1987), p. 397
 23. K. S. Johnson and R. L. Petty, *Anal. Chem.*, **54**, 1185 (1982).
 24. J. F. Tyson, *Quim. Anal.*, **8**, 171 (1989).
 25. J. F. Tyson, *Analyst*, **115**, 587 (1990).
 26. S. J. Chalk and J. F. Tyson, *Anal. Chem.*, submitted (under revision).

Practical Problems

However, there are good practical reasons for choosing one manifold design over another. One of the problems associated with spectrophotometric determinations by FI is the degradation in detection limit which occurs because of substantial refractive index peaks. Any optimization strategy aimed at achieving the best detection limits (clearly maximizing the sensitivity is one part of this design) must take into account these refractive index effects. The double line design is clearly superior to the other designs in this respect [27]. However, the double line manifold brings a source of noise not encountered with the single line designs, namely the mixing noise due to imperfect mixing at the confluence point. This is a non-trivial problem, which has not attracted the attention it deserves in the practical FI literature. In addition to the appropriate design of confluence geometry [28], it is necessary to induce secondary flow patterns to promote radial mixing downstream of the confluence point. Various reactor designs may be used including, packed beds, single bead strings, tightly coiled open tubes and knotted tubes. The use of pulse dampers should also be considered.

Exploiting the Unique Features of Flow Injection

Although much of the previous discussion of concepts and misconceptions has been based on the thermodynamics of reaction chemistry performed when solutions are mixed by controlled hydrodynamic processes, it is the kinetic features of flow injection that lead to some of the more exciting possibilities for use in novel analytical chemistry procedures. The precise timing of FI methodology means that it is an appropriate choice for performing many electrochemical determinations [29] and it has, to some extent, revived an interest in the use of chemiluminescent procedures [30] and may be used in a number of ways in kinetic methods of analysis [31,32,33]. The concentration gradients produced under conditions which allow simple concentration time relationships to be exploited (such as the exponential gradients of a well-stirred mixing chamber) can also form the basis of novel analytical procedures based on peak width [34]. Under appropriate conditions the doublet peaks, referred to earlier as a disadvantage, can be exploited for analytical purposes [35,36].

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27. J. F. Tyson and A. B. Marsden, *Anal. Chim. Acta*, **214**, 447 (1988).
 28. G. D. Clark, J. M. Hungerford and G. D. Christian, *Anal. Chem.*, **61**, 973 (1989).
 29. K. Stulik and V. Pacakova, *Electroanalytical Measurements in Flowing Streams*, Ellis Horwood, Chichester, 1987.
 30. I. M. Warner and L. B. McGown, *Anal. Chem.*, **64**, 343R (1992).
 31. H. A. Mottola and D. Perez-Bendito, *Anal. Chem.*, **64**, 407R (1992).
 32. G. D. Christian and J. Ruzicka, *Anal. Chim. Acta*, **261**, 11 (1992).
 33. E. H. Hansen, *Anal. Chim. Acta*, **261**, 125 (1992).
 34. J. J. Jordan, S. H. Hoke and H. L. Pardue, *Anal. Chim. Acta*, **272**, 115 (1993).
 35. M. K. Carroll and J. F. Tyson, *J. Chem. Educ.*, **70**, A210 (1993).
 36. R. T. Echols and J. F. Tyson, *Anal. Chim. Acta*, in press.

A basic feature of FI is that the kinetic limitations of conventional methodology can be relaxed. This concept has yet to be fully exploited in the design of reaction chemistry for FI methods, though the possibilities have been convincingly demonstrated. For example, optimization of a spectrophotometric procedure for the determination of a pharmaceutical compound produced an enhancement in sensitivity of a factor of 6 when an unstable initially formed product was monitored [37]. In a similar fashion, a 60-fold increase in sensitivity was obtained from a method for the determination of cyanide [38]. Spectacular enhancements (up to 350-fold) were obtained by Ishibashi and co-workers for the measurement of the transient potential change induced in an iron^{III}/iron^{II} buffer on the addition of various oxidative species [39,40].

Concluding Remarks

There are still some misconceptions concerning the basic phenomena of dispersion and reaction in flow injection systems being perpetrated in the literature. Authors are encouraged to be rigorous in their approach to optimization studies with the figure of merit clearly stated. Deviations from the rigorous approach based on subjective evaluations of the various practical problems are to be discouraged. Values of dispersion coefficients should always be quoted. It is clear that the controlled kinetic nature of FI methodology opens some intriguing possibilities for the development of new analytical procedures. Professor Ishibashi's excellent work is a clear indication that the full possibilities of the concept of FI have yet to be realized.

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37. D. Betteridge, T. J. Sly, A. P. Wade and J. E. W. Tillman, *Anal. Chem.*, **55**, 1292 (1983).
 38. Z. Zhu and Z. Fang, *Anal. Chim. Acta*, **198**, 25 (1987).
 39. N. Ishibashi, T. Imato, H. Ohura and S. Yamasaki, *Anal. Chim. Acta*, **214**, 349 (1988).
 40. N. Ishibashi, T. Imato, S. Yamasaki and H. Ohura, *Anal. Chim. Acta*, **261**, 405 (1992).